Improvements in or relating to the manufacture of coated polymeric substrates

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Abstract of **GB 856329 (A)**

Graft polymers are produced by irradiating a shaped polymeric substrate with at least 0,01 watt-sec./cm2 of substrate surface of ionizing radiation in the presence of 1013 to 5 X 1016 molecules of oxygen/cm2 of substrate surface and subsequently contacting the irradiated substrate with a chemically distinct, unsaturated, polymerizable monomer with no additional access of oxygen. The polymeric substrate may be of polyethylene, polystyrene, polybutadiene, rubber, polyisobutylene, a butadiene-styrene capolymer, polyvinyl chloride, fluoride or acetate, polyvinylidene chloride, polychloroprene, polytetrafluorethylene, polymethyl methacrylate, polyethylene terephthalate, polyvinyl alcohol, cellulose, regenerated cellulose, polytetrahydrofuran, polyformaldehyde, a dioxolane polymer, a phenol-, urea- or triazine-formaldehyde condensation polymer, a polyamide or polyimide, polyacrylonitrile, a polyvinyl acetal, cotton, wool or silk, and may be in the form of a knitted or woven fabric, film, fibre, tube, pipe beading, tape, extruded moulding, wire covering or powder. The monomer may be vinyl chloride, fluoride, benzoate or acetate, vinylidene chloride, tetrafluoroethylene, acrylonitrile, methacrylonitrile, an alkyl acrylate, chloroacrylate or methacrylate, propiolic acid, phenyl propiolic acid, ethyl propiolate, styrene, methyl styrene, chlorostyrene, butadiene, isoprene, chlorobutadiene, a vinyl ketone or vinyl ether or divinyl ether. Irradiation may be by particle radiation such as accelerated electrons or by electromagnetic radiation such as X-rays. Reference has been directed by the Comptroller to Specification 809,838.ALSO:Graft polymers are produced by irradiating a shaped polymeric substrate with at least 0.1 watt-sec./cm.2 of substrate surface of ionizing radiation in the presence of 1013 to 5 X 1016 molecules of oxygen/cm.2 of substrate surface and subsequently contacting the irradiated substrate with a chemically distinct, unsaturated polymerizable monomer with no additional access of oxygen (see Group IV(a)). Reference has been directed by the Comptroller to Specification 809,838.

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in or relating to the Manufacture of Coated Polymeric Substrates

We, E. I. Du Pont de Nemours & Company, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington 98,
5 State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and
10 by the following statement: —

This invention is concerned with processes for preparing coated polymeric substrates and in particular with an improvement in or modification of Specification No. 801,531.
15 Polymers of the type known as graft polymers may be prepared by irradiating a substrate of a preformed polymer and contacting the irradiated substrate with a monomer which then polymerises to form a polymer different
20 from that used as the substrate. The polymerisation of the monomer is evidently caused by free radicals formed in the original polymer. The product is a composite consisting of the substrate to which a second polymer is
25 substantially integrally attached.

In one process, the substrate is irradiated while in contact with the monomer. An undesirable feature of this process is that part of the monomer polymerises by itself with-
30 out becoming attached to the substrate. Preferably, therefore, alternate processes are employed in which the substrate is first irradiated and then contacted with the monomer.

If the initial irradiation is carried out in
35 the presence of air or oxygen, great loss of activity occurs, particularly when any appreciable interval lapses between irradiation and contact with the monomer. This loss is not complete because the oxygen contacting the
40 irradiated substrate forms peroxides which themselves act to some extent to initiate polymerisation. The activity of the peroxide is,

however, much less than that of the irradiated substrate.

In the process disclosed in the specification 45 of Specification No. 801,531 the shaped polymeric substrate is irradiated with high energy particle irradiation and substantially immediately thereafter the surface is contacted with an ethylenically unsaturated liquid monomer, 50 to form a polymeric coating on the substrate.

It has now been found that the polymeric substrate can be irradiated so as to produce free radicals therein in such a manner as to avoid deactivation of the free radicals. 55

In the process of the present invention, the polymeric substrate is irradiated with at least 0.01 watt-sec./cm² of substrate surface of ionising radiation in the presence of 10^{13} to 5×10^{16} molecules of oxygen/cm² of sub- 60 strate surface and subsequently stored, if desired, and then contacted with the desired monomer without access to any additional quantity of oxygen.

In a preferred embodiment of the invention, 65 a shaped organic polymer chosen as the substrate for the graft polymer is exposed to at least 0.01 watt-sec./cm² of ionising radiation in the presence of $10^{15}-5 \times 10^{16}$ molecules of oxygen/cm.² of surface, is then stored, if 70 necessary, at 0—50° C., in the absence of more oxygen than that mentioned, and is finally contacted with a suitable ethylenically-unsaturated, polymerisable monomer again in the absence of additional molecular 75 oxygen.

While there is no intention of being limited by the following explanation, it is believed that the present process depends upon chemical bonding between the polymeric sub- 80 strate and its polymerised coating material (which differs chemically from the substrate). Irradiation of polymeric materials tends to effect formation of the free radicals men-

tioned above. It is believed that these free radicals are formed in and on the surface of the uncoated polymeric substrate, and that they are preserved during the storage step. In the contacting step of the present process they serve as polymerisation initiators, whereby polymeric chains are grown and expanded to form a high molecular weight polymeric attachment or coating chemically bonded to the substrate. Only those free radicals which can be reached by the polymerisable monomer (i.e., those on or near the surface of the substrate) are active in the present invention. The presence of oxygen in excess of 5×10^{16} molecules/cm.^{2} of polymer surface during irradiation and/or storage destroys the effect of irradiation in the present invention.

Shaped organic polymers suitable for treatment include any normally solid organic polymeric material, especially those with molecular weights in excess of 500 and more especially in excess of 1000. The polymers may be oriented or unoriented. Thus, there may be employed hydrocarbon polymers, such as polyethylene, polystyrene, polybutadiene, rubber, polyisobutylene and butadiene/styrene copolymers; halogenated hydrocarbon polymers, such as polyvinyl chloride, polyvinylidene chloride, polychloroprene, polytetrafluoroethylene and polyvinyl fluoride; ester-containing polymers, such as polyvinyl acetate, polymethyl methacrylate and polyethylene terephthalate; hydroxyl-containing polymers, such as polyvinyl alcohol, cellulose and regenerated cellulose; ether-containing polymers, such as solid polytetrahydrofuran, polyformaldehyde and dioxolane polymers; condensation polymers, such as phenol-formaldehyde polymers, urea-formaldehyde polymers, triazine-formaldehyde polymers, polyamides and polyimides; polyacrylonitrile, polyvinyl acetals and mixtures or copolymers based on two or more of the above compounds as well as natural polymers such as cotton, wool and silk.

The shape of the organic polymer employed as a substrate in the present invention is not critical. It may be a woven fabric as illustrated in the examples which follow. Also, it may be a film, moulded object, fibre, knitted fabric, tube, pipe, beading, tape, extruded moulding, wire covering or powder. Of particular advantage are films, fibres, fabrics, and various extruded forms since they are readily adapted to continuous operation according to the process of this invention. Shaped polymers in these forms may be unrolled or extruded into the path of ionising radiation and then either run substantially immediately into contact with the polymerisable monomer or wound up and contacted with the polymerisable monomer in a separate treatment.

Monomers suitable for use in the contacting step of the present invention are un-saturated, polymerisable monomers chemically distinct (i.e., give a different polymer) from the polymer of the substrate being coated. There are included those monomers containing at least one unit of carbon-to-carbon unsaturation of either the ethylenic or acetylenic type. Thus, there may be employed vinyl chloride, vinylidene chloride, vinyl fluoride, tetrafluoroethylene, vinyl acetate, vinyl benzoate, acrylonitrile, methacrylonitrile, alkyl acrylates, alkyl chloroacrylates, alkyl methacrylates, propiolic acid, phenylpropiolic acid, ethyl propiolate, styrene, methyl styrene, chlorostyrene, butadiene, isoprene, chlorobutadiene, vinyl ketones, vinyl ethers and divinyl ether.

Suitable ionising radiations include both radiation in the form sometimes regarded as particle radiation and radiation in the form sometimes regarded as ionising electromagnetic radiation.

By " particle radiation " is meant an emission of accelerated electrons or nuclear particles such as protons, neutrons, alpha-particles, deuterons or beta-particles, so that the said particle impinges upon the shaped organic polymer. The charged particles may be accelerated by means of a suitable voltage gradient, using such devices as a cathode ray tube, resonant cavity accelerator, a Van de Graaff accelerator or a Cockcroft-Walton accelerator, as is well known to those skilled in the art. Neutron radiation may be produced by suitable nuclear reactions, e.g., bombardment of a beryllium target with deuterons or alpha-particles. In addition, particle radiation suitable for carrying out the process of the invention may be obtained from an atomic pile, or from radioactive isotopes or from other nautral or artificial radioactive materials.

By " ionising electromagnetic radiation " is meant radiation of the type produced when a metal target (e.g., tungsten) is bombarded by electrons possessing appropriate energy. Such radiation is conventionally termed X-ray. In addition to X-rays produced as indicated above, ionising electromagnetic radiation suitable for carrying out the process of the invention may be obtained from a nuclear reactor (" pile ") or from natural or artificial radioactive material. In all of these latter cases the radiation is conventionally termed gamma rays.

It is recognised that the energy characteristics of one form of ionising radiation can be expressed in terms which are appropriate for another form. Thus, it is acceptable to refer to energy equivalents between, for example, radiation commonly considered as particle radiation and radiation commonly considered as wave or electromagnetic radiation. In the process of this invention radiation which has an energy equivalent of an electron beam of at least 0.000015 Mev may be employed and beam energies in excess of 0.00005 Mev are preferred. Radiation with

energy equivalent to an electron beam of 0.00005 to 0.1 Mev is preferred where radiation of this energy is available at low cost and time is not a primary factor in the economic aspect of the process. Radiation with energy equivalent to an electron beam of 0.1 Mev and over (i.e., 0.1 Mev up to 2 to 5 Mev) is preferred where the cost of the higher intensity radiation may be offset by the saving in exposure time. This is especially true in continuous operation. Radiation with higher energies (i.e., 10 Mev and higher) may also be employed.

A minimum exposure of at least 0.01 watt-sec./cm^2 at the surface is necessary since lower degrees of exposure do not give adequate activation of the surface toward the bonding of the polymerisable monomer. The weight of the coating formed in the contacting step usually increases with increasing degrees of exposure. Upper exposure limits depend on the degree of bonding desired and on the radiation resistance of the polymeric substate. Exposures as high as 1000 to 10000 watt-sec./cm^2 may be utilised in coating radiation-resistant polymers such as polystyrene and polyethylene terephthalate, whereas exposures of 100 to 1000 watt-sec./cm^2 may suffice for more sensitive polymers such as polyvinyl chloride and the polyamides. The exposure may be carried out in one slow pass, or in several faster ones and may be conducted at any convenient amperage.

While a vacuum is the preferred means for limiting the access of oxygen to the irradiated shaped polymer, other means may be employed. For example, an inert gas, such as nitrogen, argon, helium or the like, containing molecular oxygen within the limits prescribed above, at atmospheric pressure, will serve the desired purpose.

The monomer may be gaseous or liquid when contacted with the irradiated substrate. It is particularly important that the contacing step should not involve admitting additional oxygen to the system. This is true whether contacting takes place at sub-atmospheric pressures of about 10—100 mm. of mercury or at higher pressures, e.g., up to atmospheric pressure, which can be employed when oxygen concentration is controlled by dilution with an inert gas. Preferably the pressure of the monomer is substantially identical with that over the substrate when they are contacted. Alternatively, aqueous or other solutions of the monomer or, in fact, pure liquid monomer can be used. Control of the reaction is less easy when the monomer is liquid or in solution.

The temperature of contact between irradiated substrate and monomer is not critical. Ambient temperature is convenient and hence preferred. If, however, storage of the substrate is employed, temperatures down to 0° C. or even lower are desired. To avoid loss

of activity of the free radicals, the temperature of contact should not, in any case, rise above the crystalline melting point of the substrate. In general, contact temperatures below 100° C. are preferred, although in some cases temperatures in the range of 100—200° C., may be employed when the contact time is short.

An important advantage of this invention is that the irradiation of the shaped organic polymer may be carried out under conditions best adapted for irradiation as in an atomic pile or under the influence of a particle accelerator. The contacting step may be carried out later under conditions best adapted for it and free of radiation hazards and the often-cumbersome radiation apparatus. Also, with this process radiation-sensitive, unsaturated monomeric grafting materials need not be exposed to the radiation.

The process of the present invention is valuable in creating surface effects upon shaped articles produced from organic polymers. It may be employed upon textiles to effect softness, resilience, tendency to shrink, static propensity, dyeability, pilling, hydrophilicity, wickability, and the like. It is useful in varying such properties as abrasion and wear resistance, moisture regain, dry-cleaning properties, light durability, soil-ability, ease of soil removal, laundering properties, dyeability (depth, rate, permanence and uniformity), printability, washfastness of dyes or finishing treatments (resins, ultra-violet absorbers, etc.), handle and drape properties (stiffening or softening), heat-yellowing, snag resistance, ease in textile processability, solubility (insolubilisation or increase in solubility), bleachability, surface reactivity, delustering action, drying properties, thermal and electrical conductivity, transparency, light transmittance, air and water permeability, fabric comfort, felting, ion exchange properties, adhesion, over-all appearance and combinations of these as well as others.

The invention is illustrated by the following examples; parts stated are by weight and pressures are in millimetres of mercury except where otherwise specified.

EXAMPLE I.

A glass vessel containing air and about 1.5 parts of dry 66 nylon fabric and 2 parts of dry polyethylene terephthalate fabric (both fabrics woven from filaments of about 3 denier) was evacuated to an absolute pressure of 1 mm. and sealed. The free space in the vessel was such that this pressure corresponded to 7.8×10^{16} molecules of oxygen/ g. of fabric which in turn corresponded to 4.2×10^{13} molecules of oxygen/cm.^{2} of fibre surface. The wall thickness of the vessel was 0.24 g./cm.^{2}. The vessel was exposed to 125 watt-sec./cm.^{2} of 2 Mev electrons from a Van de Graaff accelerator. The thickness

of the fabric was such that all of the fibres were within range of the electrons.

After irradiation, the vessel and contents were stored for 24 hours at room temperature. The vessel was then evacuated to 0.05 mm. pressure and opened to a similarly evacuated system containing degassed liquid methyl acrylate. The fabrics were thus in contact with methyl acrylate vapour. Light was excluded and the reaction between the fabrics and the methyl acrylate vapour was allowed to proceed at room temperature for 15 hours. The fabrics were removed from the vessel and extracted with acetone in a Soxhlet extractor for 15 hours to remove excess monomer and surface polymer not firmly attached to the fabric. The fabrics were rinsed in water and conditioned at 50% relative humidity and 23° C. The nylon fabric was found to have gained 274% in weight and the polyethylene terephthalate fabric had gained 166% in weight.

The fabrics were much stiffer, tighter and drier in hand than before the treatment. They were much less readily penetrated by water and hence much more suitable for such uses as tenting and tarpaulins than the original fabrics.

In a control experiment a nylon fabric was treated similarly except that it was not irradiated. After exposure to methyl acrylate vapours for 15 hours, the fabric had increased in weight only 0.6%.

EXAMPLE II.

The procedure of Example I was repeated except that, prior to irradiation, the air in the vessel was exhausted only to an absolute pressure of 10 mm. This pressure is equivalent to 7.8×10^{17} oxygen molecules/g. of fibre or to 4.2×10^{14} molecules of oxygen/cm² of fibre surface. During the 15 hours of contact between the fabrics and the methyl acrylate vapour, the supply of liquid methyl acrylate was exhausted. After conditioning, the nylon fabric was found to have gained 121% in weight and the polyethylene terephthalate fabric had gained 176% in weight.

EXAMPLE III.

A nylon fabric woven from 3-denier fibres was treated in the manner of Example I except that the air pressure in the vessel prior to irradiation was 25 mm. corresponding to 5×10^{18} molecules of oxygen/g. of fibre which in turn corresponds to 2.7×10^{15} molecules of oxygen/cm² of fibre surface. At the end of the procedure the fabric had gained 250% in weight.

EXAMPLE IV.

A nylon fabric was treated as in Example 1 except that the air pressure in the vessel prior to irradiation was 50 mm. Based on the free space in the vessel, this pressure correspond to 1×10^{19} molecules of oxygen/g of fibre or to 5.4×10^{15} molecules of oxygen/ cm² of fibre surface. At the end of the treatment the fabric had gained only 2.5% in weight.

EXAMPLE V.

The process of Example IV was repeated except that the air pressure in the vessel prior to irradiation was 99 mm. This corresponds to 2×10^{19} molecules of oxygen/g. of fibre which in turn corresponds to, 1.1×10^{16} molecules of oxygen/cm² of fibre surface. At the end of the treatment the fabric had gained 1% in weight.

It will be readily appreciated that the surface area of a given weight of shaped organic polymer will vary with the particular shape employed. In a given space employed for carrying out irradiations according to this invention, an oxygen content which has little effect on bonding of a coating to a given weight of polymer in the form of very fine fibres might be sufficient to destroy all the bonding activity in the same weight of the same polymer in the form of a moulded object with substantially lower surface area.

In Example III there is shown the irradiation of a fabric woven from 3 denier nylon fibres in a container which at 25 mm. absolute pressure of air contains 2.7×10^{15} molecules of oxygen/cm² of fibre surface. If nylon fabric of the same weight but woven from 1 denier fibres is treated in the same container at the same pressure, the ratio is 1.6×10^{15} molecules of oxygen cm² of fibre surface. If the nylon is in the form of a film 0.006″ thick of the same weight and is treated under the same conditions, the ratio is 4.4×10^{16} molecules of oxygen/cm² of film surface. This is shown along with data for other shapes of polymer and other pressures for conditions otherwise like those of Example III:—

Fibre denier or film thickness	Surface area/g.	Molecules O_2 per cm² at pressure of			
		1 mm.	25 mm.	50 mm.	99 mm.
1	3170 cm²	2.5×10^{13}	1.6×10^{15}	3.2×10^{15}	6.3×10^{15}
3	1850	4.2×10^{13}	2.7×10^{15}	5.4×10^{15}	1.1×10^{16}
5	1430	5.5×10^{13}	3.5×10^{15}	7.0×10^{15}	1.4×10^{16}
3 mil film	230	3.4×10^{14}	2.2×10^{16}	4.4×10^{16}	8.7×10^{16}
6 mil film	115	6.8×10^{14}	4.4×10^{16}	8.8×10^{16}	1.7×10^{17}

It will be noted that with both of the film shapes at 99 mm. air pressure and with the 0.006″ film at 50 mm. air pressure, the maximum ratio of 16 oxygen molecules/cm² of polymer surface for good bonding (5×10^{16}) is exceeded. The lower limit of 10^{13} molecules of oxygen/cm.² of polymer surface represents a practical lower limit below which the cost of maintaining the low oxygen content offsets the advantages of the present invention.

WHAT WE CLAIM IS:—

1. The process of producing a graft polymer which comprises irradiating a shaped polymeric substrate with at least 0.01 watt-sec./cm.² of substrate surface of ionising radiation in the presence of 10^{13} to 5×10^{16} molecules of oxygen/cm.² of substrate surface and subsequently contacting the irradiated substrate with a chemically distinct, unsaturated, polymerisable monomer with no additional access of oxygen and thereby polymerising the monomer on the surface of said substrate.

2. A process according to Claim 1 in which the ionising radiation is particle radiation.

3. A process of Claim 2 in which the ionising radiation is accelerated electrons.

4. A process according to Claim 1 in which the ionising radiation is electromagnetic radiation.

5. A process according to Claim 4 in which the ionising radiation is X-rays.

6. A process according to any of the preceding claims in which the energy of the ionising radiation is at least 0.000015 Mev.

7. A process according to any one of the preceding claims in which the polymeric substrate has a molecular weight in excess of 500.

8. A process according to Claim 7 in which the polymeric substrate has a molecular weight in excess of 1000.

9. A process according to any of the preceding claims in which the substrate is a polyamide.

10. A process according to Claim 9 wherein the polyamide is nylon.

11. A process according to Claims 1 to 8 in which the substrate is a polyester.

12. A process according to Claim 11 wherein the polyester is polyethylene terephthalate.

13. A process according to any of the preceding claims wherein the polymerisable monomer is an ethylenically unsaturated monomer.

14. A process according to Claim 13 in which the monomer is methyl acrylate.

15. A process according to any of the preceding claims in which the substrate is in the form of a film, fibre, fabric or extruded structure.

16. A process according to any of the preceding claims when carried out in the presence of $10^{15} - 5 \times 10^{16}$ molecules of oxygen/sq. cm. of substrate surface.

17. A process according to Claim 1 wherein the pressure of the polymerisable monomer is substantially identical with that over the substrate when they are contacted.

18. A process according to Claim 1 when carried out substantially as described in any one of Examples I to V.

19. Graft polymers when prepared by the process claimed in any one of the preceding claims.

20. Graft polymers formed in accordance with any of Claims 1 to 18 by condensing gaseous methyl acrylate onto nylon irradiated with at least 0.01 watt-sec./cm.² of surface of ionising radiation.

21. Graft polymers formed in accordance with any of Claims 1 to 18 by condensing gaseous methyl acrylate onto polyethylene terephthalate irradiated with at least 0.01 watt-sec./cm.² of surface of ionising radiaion.